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Supercritical fluid (SCF) extraction has been investigated for the production of the mesophase pitch used to spin high-performance carbon fibers. A bench-scale, continuous-flow apparatus was designed and constructed for fractionating petroleum pitch with SCF solvents at temperatures and pressures to 400 °C and 350 bar, respectively. A heat-soaked, isotropic petroleum pitch has been fractionated with supercritical toluene in a region of liquid-liquid equilibrium at temperatures and pressures from 300-380 °C and 30-140 bar, respectively. Bottom-phase pitch fractions produced at 340 °C, 70 bar, and a toluene-to-pitch ratio of 3:1 consist of a 100% bulk mesophase. This mesophase has been used to produce carbon fibers with strengths and moduli (3.3 and 820 GPa, respectively) equal to or better than the best pitch-based fibers currently available. Since SCF extraction can be used to produce mesophase on a continuous basis, production costs could be as low as \$0.50/lb. For high production rates of carbon fiber, this processing technique would have a significant cost advantage over alternative methods for producing mesophase.

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SUPERCritical FLUID EXTRACTION: A NEW PROCESS FOR
PRODUCING HIGH-PERFORMANCE, LOW-COST CARBON FIBERS

FINAL REPORT

MARK C. THIES

APRIL 1, 1992

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FOREWORD

Although mesophase pitch-based fibers were originally expected to be an economical high-performance material, this has not yet proven to be the case. In this study, we investigated a new technique for preparing the mesophase precursor for pitch-based fibers, which has the potential to dramatically reduce overall fiber production costs. We believe that supercritical fluid (SCF) extraction not only can be used to produce a more economical mesophase precursor, but also has inherent advantages which can lead to fibers with improved strengths and moduli, and with extremely high thermal conductivities. These fibers, when used in composites, will allow increased design flexibility by controlling the higher heat loads and fluxes which will exist on advanced electronic devices, aircraft, and spacecraft.

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Statement of Problem

High-performance carbon fibers can be produced from either of two organic precursor materials: polyacrylonitrile (PAN) or petroleum pitch. PAN-based fibers generally exhibit higher strengths (because of their fibrillar nature), whereas mesophase pitch-based fibers have higher moduli (because of their more graphitic structure).

Although mesophase-based fibers were originally touted as the first low-cost, high performance carbon fibers (1), this has not proven to be the case. In fact, as shown in Table I, the average cost of mesophase-based fibers is still higher than for the PAN-based products. This situation exists in spite of the fact that the raw material costs for mesophase-based fibers are significantly lower and product yields are significantly higher.

Table I. Cost of PAN- and mesophase-based carbon fibers (1).

	Cost of Precursor (\$/lb)	Cost of Carbon Fibers (\$/lb)
PAN-based	0.18	27
mesophase-based	0.11	40

The cost of preparing the mesophase is generally acknowledged to be a major factor in the higher selling price for mesophase-based fibers. Recent estimates (2) indicate that preparing mesophase by the conventional heat-soaking process may cost as much as \$10/lb of finished product, which is almost half of the total cost of making mesophase-based fibers. In addition, depending on the quality of the mesophase, spinning conversion and oxidation costs may also be higher than for PAN-based fibers.

In addition to its high cost, the conventional heat-soaking process for preparing mesophase has several deficiencies which limit its ability to produce an improved mesophase pitch:

1. Mesophase pitch produced by this process has a wide molecular weight distribution (MWD), and this MWD cannot be readily controlled (3,4). Recent work by researchers such as Mochida has demonstrated how significantly the MWD can affect the physical properties of the mesophase pitch (3,5-7).
2. In the production of mesophase pitch by heat soaking, the product is the residual portion of the feed pitch. Therefore, any nonvolatile impurities in the pitch such as coke dust or mineral matter which are not completely removed by filtration remain in the final product. These impurities cause defects in the resulting fibers which adversely affect properties such as tensile strength (8,9).
3. Producing mesophase by heat soaking is a batch process. With batch processes, there are always concerns regarding batch-to-batch variations in product consistency, particularly if there are unexpected changes in the feed material (in this case, the isotropic pitch). Another problem

with batch processes is that they are relatively expensive to operate on a unit-cost basis. In general, the lowest production costs are achieved with continuous processes.

In recent years, the Japanese have made significant advances in the production of mesophase pitches with improved physical properties. Probably the best product produced to date is the Mitsubishi AR mesophase pitch, which is expected to become commercially available by next year. AR mesophase is produced by the catalytic polymerization of naphthalene with HF and BF_3 (3,5). Edie has recently demonstrated how AR mesophase can be used to produce fibers with properties significantly superior to those obtained from heat-soaked mesophase (10). Although AR mesophase is an excellent product, it also has disadvantages:

1. As a raw material, naphthalene is several times more expensive than petroleum pitch. These higher raw material costs will limit just how cheaply AR mesophase can be made.
2. AR mesophase is produced by a batch process.
3. Another potential problem is the use of HF as a catalyst. Chemical companies in this country are under pressure to eliminate the use of HF in their processes. Thus, whether AR mesophase would be produced in this country is uncertain.

In summary, petroleum pitch has tremendous potential as an inexpensive raw material for the production of mesophase pitch-based fibers, but its advantages have not yet been realized. In this study, we investigated a new process, SCF extraction, for producing an economical and improved mesophase from petroleum pitch.

Significant Results

A chronological listing of our most significant accomplishments for each reporting period of this contract is shown below.

February 1, 1989. Began research contract. Continued design and construction of SCF extraction, continuous-flow apparatus for fractionating isotropic petroleum pitch.

June 30, 1989. Modified apparatus to reliably pump molten pitch, to prevent pitch precipitation, and to improve reliability of sample collection of pitch. Purchased GPC and VPO; acquired part ownership of new NMR in Chemistry. Determined phase boundaries for mixtures of supercritical toluene and Ashland A-240 pitch in a vapor-liquid region at 360 °C, at pressures up to 40 bar, and at a S/F ratio of 2:1.

December 31, 1989. Measured vapor-liquid equilibria for model systems phenanthrene/toluene and tetralin/toluene to verify operation of apparatus and estimate phase behavior for pitch/toluene mixtures. Measured vapor-liquid equilibrium (VLE) compositions for toluene/A-240 pitch systems at 320, 360, and 400 °C for pressures from approximately 30 to 80 bar at a S/F ratio of 2:1. Measured MWD of top- and bottom-phase compositions by GPC. Was not able to produce mesophase pitch at any conditions of VLE.

June 30, 1990. Analyzed pitch fractions produced in VLE region by VPO, GPC and elemental analysis, and by ^1H and ^{13}C NMR. Calculated average molecular structures and parameters for the feed pitch and for each fraction produced. Results indicated SCF extraction was effective in fractionating petroleum pitch by molecular weight. Discovered a liquid-liquid region at 360 °C and 70-110 bar in which the bottom phase contained about 25% mesophase. Both A-240 and a Conoco pitch were used as feed pitches. Began search for a nonvisual technique to detect the liquid-liquid interface in the opaque region where mesophase was produced.

December 31, 1990. Developed a capacitance technique to locate the liquid-liquid equilibrium region for mixtures of Conoco pitch and supercritical toluene. Designed and constructed an impedance bridge for monitoring the level in the equilibrium cell. Fractionated isotropic Conoco pitch with supercritical toluene in a region of liquid-liquid equilibrium at 305, 340, and 380 °C at pressures to 125 bar and a S/F ratio of 3:1. Most bottom-phase samples collected contained a high percentage of mesophase. Demonstrated that SCF extraction has the ability to control the composition of mesophase. Analyzed the solvent-soluble portion of mesophase by NMR and GPC.

June 30, 1991. Continued fractionation work discussed above. Tested physical properties of mesophase-containing fractions to determine suitability for spinning, including softening points and viscosity-shear rate data at various temperatures. Attempted to spin four pitch fractions into fibers. Two fractions would not melt and two were spun with difficulty. The spun fractions were oxidized, carbonized, and tested for final mechanical properties. Good moduli were obtained but strengths were low.

December 31, 1991. Produced about 50 g of mesophase pitch at 340 °C, 70 bar, and S/F ratio of 3:1. After devolatilization to remove residual toluene, the pitch was found to consist of a continuous, 100% bulk mesophase. This mesophase was melt-spun, oxidized, and carbonized, and the resultant fibers were found to have strengths and moduli equal to the best fibers currently available. (see Table II). XRD and SEM analyses indicate that our fibers have a highly oriented microstructure and high thermal conductivities.

Table II. Properties of carbon fibers spun from different mesophases.

Mesophase Type	Fiber Diameter (μm)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation to Failure (%)
Heat-soaked	12.1 ± 0.6	2.2 ± 0.4	360 ± 80	0.62 ± 0.18
Exptl Japanese	7.0 ± 0.3	3.1 ± 0.8	800 ± 160	0.48 ± 0.09
SCF-extracted	9.0 ± 0.4	3.3 ± 1.1	820 ± 230	0.58 ± 0.16

Gauge Length = 10.0 mm

Number of Filaments Tested = 30-40

List of Publications

1. Hutchenson, K. W., J. R. Roebers, and M. C. Thies, "Fractionation of Petroleum Pitch by Supercritical Fluid Extraction," *Extended Abstracts*, Nineteenth Biennial Conference on Carbon, State College, PA, June 1989; p. 218-9.
2. Hutchenson, K. W., J. R. Roebers, and M. C. Thies, "Fractionation of Petroleum Pitch by Supercritical Fluid Extraction," *Fiber-Tex '89: The Third Conference on Advanced Engineering Fibers and Textile Structures for Composites*, Greenville, SC, October 1989; Buckley, J. D., Ed; NASA Conference Publication 3082; pp. 71-81.
3. Hutchenson, K. W., J. R. Roebers, J. C. Mullins, and M. C. Thies, "Phase Equilibria for Mixtures of Petroleum Pitch and Supercritical Toluene," *Extended Abstracts*, AIChE 1989 Annual Meeting, San Francisco, CA, November 1989; Abstract 169 Am.
4. Roebers, J. R. and M. C. Thies, "An Equilibrium View Cell for Measuring Phase Equilibria at Elevated Temperatures and Pressures," *Industrial & Engineering Chemistry Research*, **29**, 1568 (1990).
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